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SiO$_2$ Film Stress Distribution during Thermal Oxidation of Si

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ABSTRACT

A laser reflection technique is used to investigate the relaxation of SiO_2 film stress which occurs during the dry thermal oxidation of Si between 700° and 1000°C. Included is a determination of the stress distribution in the oxide by two independent methods: 1) measurement on oxides of various thicknesses from 100 to 800 A, and 2) repeated stress measurements on chemically thinned SiO_2 films, viz. etch back analysis toward the interface. Agreement is found between these experiments. These thin film stress measurements are achieved by the use of ultra-thin Si substrates (75 μm). Essentially, an increase in film stress with decreasing film thickness is observed. Rapid stress relaxation is observed for all temperatures studied and is attributed to a time-dependent oxide viscosity. The influence of these measured properties on the kinetics of Si oxidation is discussed.

INTRODUCTION

A number of studies have reported the observation of an intrinsic film stress resulting from the thermal oxidation of Si (1-4). The origin of this stress has been attributed to the 120% molar volume expansion which results from the conversion of Si to SiO_2. A Maxwell viscoelastic flow model (2,3,5) has been proposed to explain the occurrence of increasing stress at reduced oxidation temperatures (<950°C), where higher oxide viscosities preclude stress relaxation during normal oxidation times. Since the intrinsic stress exists at the oxidation temperature, it is possible that this stress influences the oxidation kinetics. However, there is some disagreement on whether this stress effect is more influential on the interface reaction (2,6,7) or the diffusional transport of O_2 through a growing oxide (8-10). Also, other properties such as SiO_2 film density (2,11) and electrical characteristics (12-13) may be influenced by the stress and its distribution.

We report new measurements on the SiO_2 film thickness dependence of intrinsic stress using a laser reflection technique (3). This dependence is determined by two independent experiments. In one experiment the oxidized samples are grown to various thicknesses, while the other uses oxides that are chemically etched. Concordant results are obtained and compared with present stress models. The implications of these results on related oxidation models are also discussed.

EXPERIMENTAL PROCEDURES

A.   Sample Preparation.

All experiments were performed using commercially available p-type (100) Si wafers. Wafer characteristics include a substrate thickness of approximately 75 μm (3 mil), a resistivity of 2 Ω-cm, and an initial diameter of 2 inches. Samples used for measurement were cut from the original wafers by cleaving along the major axis (100) to obtain 1x4 cm strips. A pre-oxidation at high temperature (1050°C) was performed prior to cleavage of the original wafers in order to prevent subsequent contamination by Si dust during cleaving. After removing this oxide in a concentrated HF solution, samples were cleaned using a slightly modified form of the RCA method (14) prior to the experimental oxidation.

Thermal oxidation of the Si substrates was performed at 700, 800, and 1000°C in a double-walled resistively heated fused silica tube furnace. Oxidation temperatures are reported with less than 2°C variation, and O_2 with less than 0.5 ppm hydrocarbons was used. The H_2O content of the O_2 was measured during oxidation at the furnace outlet with a hygrometer, and found to contain less than 5 ppm H_2O. A flowing N_2 ambient was maintained between the inner and outer walls of the furnace tube and inside the furnace when oxidations were not in progress. Film thicknesses were measured with an accuracy of better than 2% using a precision manual ellipsometer with a He-Ne laser (6328 A) as the source. As previously detailed (2-4), the grown SiO_2 was removed from the backside of each sample prior to the strain

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measurement, and after the measurement the substrates were rechecked for residual curvature with the oxide completely removed. Two independent experiments were performed to determine the distribution of stress in SiO_2 films. First, a series of oxides from approximately 100-800 A were grown to determine if any measurable stress relaxation occurs in the initial thin regime of Si oxidation. Stress measurements were performed independently at each thickness for the three reported temperatures. Since the measured stress is the average oxide stress integrated over the thickness (15), this experiment establishes the distribution of stress from the interface to the outer surface when a series of different thicknesses are measured. Secondly, oxides were grown to about 800 A and chemically thinned in a buffered HF solution ($NH_4F:HF/50:1$). Stress was measured after each etch on the same samples. The comparison of stresses from these two techniques yields information relative to stress relaxation during growth, since the thin oxides obtained in the first experiment are exposed to less high temperature than those obtained from the etch back method.

B. Strain measurements.

A previously reported (3,4) parallel laser reflection technique was used to study film stress as a function of oxide thickness, and only the essential features are repeated here. This technique involves a measurement of the change in the radius of curvature (R) of the Si substrate induced by stress from the SiO_2 film. The curvature change is obtained from measurements of the change of the separation of two parallel laser beams reflected from the film-substrate surface. The

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total film stress can be calculated using a form of Stoney's equation (16):

$$\sigma_f = E t_s^2 / 6(1-v) t_f R \qquad (1)$$

where t_s and t_f are the substrate and film thicknesses, respectively, and E and v are Young's modulus and Poisson's ratio, respectively, and are reported elsewhere (4). Since σ_f is measured at room temperature, it contains a thermal expansion component σ_{th} in addition to the residual intrinsic stress σ_i. σ_{th} is the result of a thermal expansion mismatch between Si and SiO_2, which upon cooling from oxidation to room temperature yields a stress that may be calculated (17) and subtracted from σ_f to obtain σ_i. The new stress results reported herein include the extension of past measurements (3) to SiO_2 film thickness below ~800 A in order to determine the stress distribution in the oxide. This extension is accomplished through the use of thin Si substrates (~75 μm), so as to yield measurable R values for small thicknesses. The reported data in both experiments was usually the average of at least 3 samples, each with multiple measurements, and resulted in an average error of ~0.5x10^9 dyn/cm^2 . The etch back results showed a larger scatter from the curves, which may be attributed to the repeated handling of the same samples during the series of etches and measurements.

RESULTS AND DISCUSSION

A. Viscous flow.

Figures 1 and 2 show the dependence of intrinsic film stress on oxide thickness for three temperatures and a range of oxide thicknesses

from ~ 100-800 A. The data in Fig. 1 was obtained by growing oxides to various thicknesses and in Fig. 2 from chemical thinning or etch back of SiO_2. Both techniques yield essentially the same result within experimental error. Considering that the thin SiO_2 samples used were exposed to decidedly different thermal budgets, the stress relaxation must be fast relative to oxidation times. This is a fundamental point and will be discussed below. Also, there is clearly a trend toward larger stress for smaller SiO_2 thicknesses. This variation with thickness is smaller for low temperature grown SiO_2 films which exhibit larger stresses. While the data does not extend to films less than 100 A, a common extrapolated value of ~4.5×10^9 dyn/cm^2 is obtained for the maximum intrinsic stress at zero SiO_2 thickness. This finding of a single value for the maximum stress is expected since the origin of stress is due to the constant molar volume change strain that occurs at the Si surface during oxidation. The value for this maximum stress is, however, smaller than expected (2) and will also be discussed further below. Finally, the stress values for thicker films are near the previously reported results for thick SiO_2 samples prepared on thicker (200 μm) Si substrates (4).

We now return to the issue of stress relaxation. According to a simple Maxwell model for a solid, viz. a spring and dashpot in series, we expect the relaxation of stress to occur by viscous motion of SiO_2 away from the Si surface. The strain rate, $d\epsilon/dt$, is expressed as:

$$d\epsilon/dt = \sigma_i/\eta \qquad (2)$$

where η is the oxide viscosity (2). Hence for smaller viscosities the strain rate is higher and relaxation occurs more rapidly. The

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equilibrium viscosity is an exponential function of temperature as
shown by the Andrade equation (18):

$$\eta = \eta_o \, \exp \, (E\eta/RT) \qquad (3)$$

where η_o is a pre-exponential constant which represents the minimum
viscosity and $E\eta$ the energy of activation for viscous flow. The
effects of equilibrium viscosities will be discussed later. The
relaxation of stress due to viscous flow in a Maxwell solid can be
summarized by the following equation:

$$\sigma_1 (t) = \sigma_o \, \exp(-t/\tau) \qquad (4)$$

where σ_o is a pre-exponential constant (maximum oxide stress directly
at the interface), t is the oxidation or annealing time (time exposed
to a given temperature), and τ the relaxation time. Relaxation times
have been predicted from viscosity measurements based on the following
equation:

$$\tau = \eta/G \qquad (5)$$

where G is the elastic shear modulus. Since G is a moderately weak
function of temperature (19) and η a strong function of temperature,
the temperature dependence of the relaxation time is strongly dependent
on the oxide viscosity.

From literature values for G (20) and extrapolated values for η
(20), relaxation times are estimated from equation (5) and presented
in Table 1. It should be noted that these constants are obtained from
measurements on bulk glass materials, and may be in error for thin SiO_2
films. The calculated τ's suggest that the stress relaxation is slow
relative to normal oxidation times for low temperatures. This is
partly substantiated by the higher stress and shallower slope of the

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relaxation curves for low temperature grown films. However, if this were entirely true then we would expect the curves in Fig. 1 to show virtually a zero slope over the oxidation time periods investigated. In addition, the etch back stress results of Fig. 2 would yield lower stress values than the individually grown samples of Fig. 1 in the thin film regime. This is due to the fact that the oxidation rates are greater in the initial regime where thin films are grown and thus less exposure to high temperature is required for the individually grown thin oxides. For example, it takes ~ 78 min. to grow a 100 Å film at 800°C, but to add 100 Å to an already grown 700 Å film requires ~ 460 min (21). This factor of 6 difference in time should enable greater relaxation of stress for the etched back 100 Å sample which grew at a substantially slower rate. Also, it should be remembered that the SiO_2 film grows via the inward migration of O_2, hence the newest oxide is added at the Si-SiO_2 interface. Since the stress values in Fig. 2 are not lower than those in Fig. 1, the growth rate must have a marked influence on the relaxation during growth. Given the large experimental error associated with the etch-back results, it is not yet clear how pronounced this effect really is.

It appears that the initial stress relaxation observed for the grown SiO_2 films is faster than one would expect from the calculated τ's reported in Table 1, with the result that there is a rapid lowering of the stress to some initial value from which there is a slower relaxation. Thus, either our experimental results cannot be understood by a simple Maxwell model, since a fast relaxation is observed for SiO_2 as it is formed under potentially higher stress in the early stages of

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oxidation, or a decidedly smaller oxide viscosity than used in Table 1 exists in thin films. The fast initial relaxation may be the result of an out of equilibrium viscosity for the newly formed layer near the Si-SiO_2 interface. This nonequilibrium situation cannot result from temperature differences, since the oxidation is isothermal, but is likely derived from time-dependent plasticity as a result of changing film thickness. As the growing layer moves away from the interface, the SiO_2 network relaxes, and an equilibrium value for viscosity is obtained. Thus two parallel relaxation phenomena are envisioned: first the initially fast, temperature independent relaxation from a maximum intrinsic stress value to a much lower value; second the Maxwell-like relaxation of the well formed and annealed SiO_2 network.

In order to model this situation, we can reconsider equation (2), which expressed the viscous flow rate, and provide a more generalized viscoelastic expression (22):

$$d\epsilon/dt = A\sigma^n \qquad\qquad (6)$$

where n is a constant. For linear theory of viscoelasticity, n=1, $A=1/\eta$, and equation (2) gives the proper form for the deformation rate (σ/η). For $1 < n < 10$, non-linear viscoelastic behavior results (22), and equation (2) must be modified. Tiller (6) has predicted a value of 2 for n based on consideration of the distance at which stress relaxes an order of magnitude, yielding a nonequilibrium structured layer near the interface. Other studies on stress relaxation in glasses have also shown n=2 (23), where greater stresses result in non-linear responses. An approach by Tan and Goesele (24) compares an initial time-dependent

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viscosity $\eta_i(t)$ in a freshly formed material to a well-annealed time-independent viscosity η_e, revising the viscous flow rate equation:

$$d\epsilon/dt \propto \sigma/\overline{\eta}_t \qquad (7)$$

where $\overline{\eta}_t$ is an average viscosity. This suggests that during oxidation, an average viscosity of the oxide over the entire thickness range must be considered rather than one of true equilibrium. A number of authors have suggested that the freshly grown oxide near the interface is probably more fluid than the oxide near the outer surface (5, 15, 24), resulting in a nonequilibrium layer near the interface. Also, the growing film may impose an additional driving force to the temperature activated viscous flow, resulting in a lower observed activation energy for this process. This force depends on the changing film thickness and growth rate, viz. a decrease in film growth velocity as the oxide moves away from the surface. These ideas seem to be consistent with our experimental results.

B.   Kinetic models related to stress.

As stated earlier, there is some disagreement in the literature on whether stress primarily effects the interface reaction (2, 6, 7) for Si oxidation or the diffusion of O_t through a strained oxide (8-10). Non-Arrhenius behavior has been observed for both the parabolic (k_p) and linear (k_l) rate constants (25-27) that are derived from the Deal-Grove oxidation model. Stress is thought to affect these constants, since a break in their activation energies occurs at approximately the viscous flow point of the oxide (950°C), where stress increases for lower oxidation temperatures.

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The stress-diffusion models (8-10) consider a change in the diffusion mechanism due to stress. Fargeix and Ghibaudo (8) have considered the effects of σ_l on k_p through a modified expression for the diffusion (D) of oxidant:

$$D = D_o \, \exp \, (-\sigma\Delta V/kT) \tag{8}$$

where the pre-exponential constant is the diffusivity through a stress free oxide, σ is the level of stress in the oxide, and ΔV is the diffusion volume change due to σ. The authors deduce a maximum oxide stress of 4.5×10^{10} dyn/cm^2 to account for the difference in the activation energies for k_p at low (<950°C, 2.2 eV) and high (>950°C, 1.3 eV) temperatures, and propose it to be constant over a wide temperature range (780-930°C). We find a maximum oxide stress at zero thickness an order of magnitude lower ($\sim4.5\times10^9$ dyn/cm^2) that appears to be independent of oxidation temperature, in agreement with the origin of stress as the constant molar volume change that occurs during oxidation. It thus appears that the observed stress is too low and therefore inconsistent with this model. However, the influence of stress on diffusion cannot be totally refuted. Recent studies have shown an increase in oxidation rate upon annealing thick oxides (28), presumably by relieving the compressive stress and increasing D. Also, a crossover is observed in oxidation rates with oxide thickness for different surface orientations (29), which appears to be the result of a change in oxidant transport due to stress. At the present time, none of these studies can be considered conclusive, hence the role of stress on transport is still in doubt, and the presently proposed models are not fully in accord with the newest stress data.

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A different approach has been taken by Irene (7) in describing the effects of stress on oxidation kinetics using a revision of the linear rate constant obtained from the Deal-Grove oxidation model (25). The following expression has been proposed:

$$k_l \ \alpha \ C_{s_i} \ \sigma_i / \eta \tag{9}$$

where C_{s_i} is the areal density of Si atoms for different Si orientations. In a recent study (4) we showed the effect of Si orientation on film stress. The lower than anticipated stress found for the (111) Si orientation and the high rate of oxidation suggests that the above expression for k_l is not correct as written. Relation (9) incorporates the viscous flow rate as a factor affecting k_l. This model considers the interface reaction to be controlled to some degree by the viscoelastic properties of the oxide which relieve the volume requirements for the conversion of Si to SiO_2. As a result, a tensile stress exists in the underlying Si, which may increase the reactivity of the Si. Recently it was reported (30) that the application of a tensile load to a Si surface during oxidation resulted in a small increase in oxidation rates for thin films (<200 A). Our present experimental data shows that much of the stress is relaxed to some nearly constant value within the first 1000 A of oxide thickness. It has been shown that k_l may be dominant even beyond 1000 A (31), and thus if stress does influence the oxidation rate significantly it is likely to alter the Si surface reaction rate constant. Since we have shown that a high stress exists in the early stages of oxidation even at 1000°C, our results demonstrate that it is possible for stress to influence oxidation kinetics even at higher temperatures (>950°C).

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SUMMARY AND CONCLUSIONS

We have reported the results of stress relaxation of dry thermal SiO_2 films on very thin Si substrates which are used to enhance the sensitivity of the measurement. Our results indicate a much faster stress relaxation during oxidation in comparison with bulk vitreous silica measurements, which may be the result of a reduced oxide viscosity and a resulting lower activation energy for viscous flow. It is believed that freshly formed oxide near the $Si-SiO_2$ interface is more fluid than that near the outer surface, and non-linear theory of viscoelasticity must be used to explain these results. We propose that a changing film growth rate alters the viscoelastic properties of a growing oxide, providing an additional driving force to viscous flow. Since this relaxation occurs mostly in the initially fast rate regime of oxidation, it is believed that intrinsic film stress may have a stronger influence on the interface reaction than on the transport of oxidant in the film, and may be important even at temperatures above the viscous flow point.

ACKNOWLEDGEMENT

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FIGURE AND TABLE CAPTIONS

Figure 1.   Intrinsic film stress distribution as a function of oxide thickness for independent samples grown to various thicknesses.

Figure 2.   Intrinsic film stress vs. oxide thickness for chemically thinned oxides, viz. etch back analysis.

Table 1.   Relaxation time constants predicted from viscosity measurements.
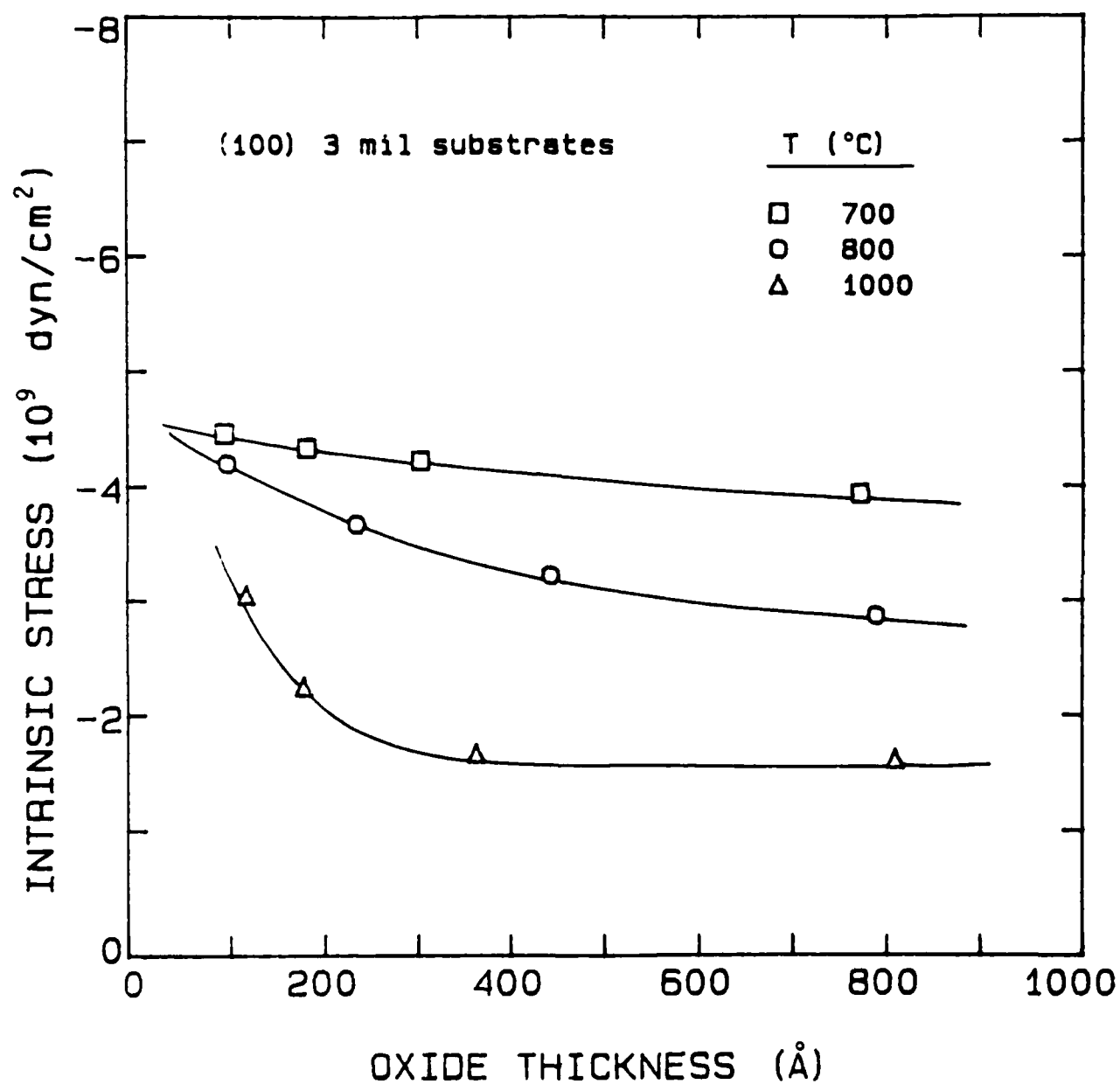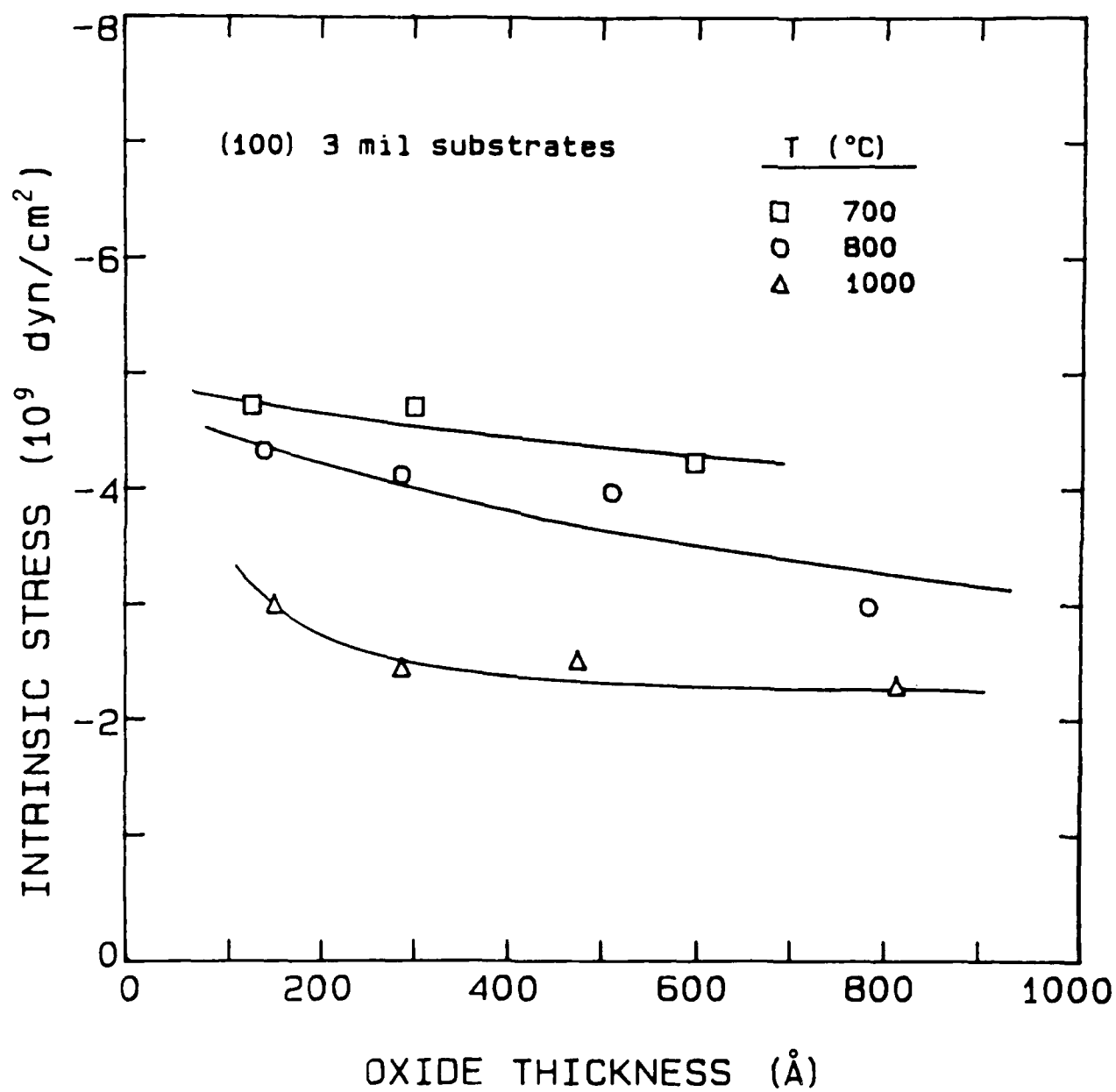
Fig. 1
Koboda + Irene

Fig. 2

Kobeda + Ir

TABLE 1. Relaxation time constants.

T (°C)	τ (s)
700	1.9×10^7
800	6.3×10^5
1000	715

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